Improvement of the Tribological Behavior of Ultra-High-Molecular-Weight Polyethylene by Incorporation of Poly (Phenyl *p*-Hydroxyzoate)

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ABSTRACT: Ultra-high-molecular-weight polyethylene/ poly (phenyl *p*-hydroxyzoate) composites (coded as UHMWPE/PPHZ) were prepared by compression molding. The effects of the poly (phenyl *p*-hydroxyzoate) on the tribological properties of the UHMWPE/PPHZ composites were investigated, based on the evaluations of the tribological properties of the composites with various compositions and the examinations of the worn steel surfaces and composites structures by means of scanning electron microscopy and transmission electron microscopy. It was found that the incorporation of the PPHZ led to a significant decrease in the wear rate of the composites. The composites with the volume fraction of the PPHZ particulates within 45% ~ 75% showed the best wear resistance. The friction coefficient of the UHMWPE/PPHZ composites decreased with increasing load and sliding velocity, while the wear rates increased with increasing load. This was attributed to the enhanced softening and plastic deformation of the composites at elevated load or sliding velocity. The UHMWPE/PPHZ composites of different compositions had differences in the microstructures and the transfer film characteristics on the counterpart steel surface as well. This accounted for their different friction and wear behaviors. The transfer film of the UHMWPE/PPHZ composites appeared to be thinner and more coherent, which was largely responsible for their better wear resistance of t composite than the UHMWPE matrix. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2336–2343, 2005

Key words: ultra-high-molecular-weight polyethylene; poly (phenyl *p*-hydroxyzoate); composite; friction and wear behavior

INTRODUCTION

Innovations in modern technology have placed ever-increased demands on advanced composite materials. Of the most commonly used composite materials in modern engineering, the polymer-matrix composites have been finding increased applications, owing to much smaller weight and better corrosion resistance and biocompatibility than the metal-matrix and ceramic-matrix composites.[1] For example, ultra-high-molecular-weight polyethylene (UHMWPE) has been widely used in bearing applications due to its good chemical stability, biocompatibility, and friction-reducing and antiwear ability.[2] It has also been used as some components or parts of machines in chemical engineering, textile engineering, transportation engineering, agricultural engineering, food processing, and the paper making industry, because of its excellent chemical corrosion resistance,

water-repellent function, adhesion resistance, and self-lubricity.[1] Specifically, UHMWPE has been applied as a material of an acetabular prosthesis component in hip and knee total joint replacement for more than 30 years.[3,4] It has been well known that the wear resistance of UHMWPE can be significantly increased by the addition of various filler to form UHMWPE composites.[5–15] Suwanprateeb said that $CaCO_3$ particulates were effective to increase the wear resistance of binary or ternary UHMWPE-based composites.[5] Xie and coworkers reported that quartz particulates acted to greatly improve the wear performance of UHMWPE.[14] Hashmi and coworkers investigated the friction and wear behaviors of the blends of UHMWPE with polyphenylene, polyamide, or polyurethane.[8]

As a novel special engineering plastic with outstanding self-lubricity, wear-resistance, insulation, thermal stability (able to flow nonviscously at a temperature up to 380°C), and radiation resistance, PPHZ has a smaller wear rate and higher thermal conductivity than conventional commercial thermoplastics, including polytetrafluoroethylene (PTFE), polyamide (PA), and polycarbonate (PC). It keeps intact to all organic solvents and has no melting point. This, to-

gether with the similar physical and mechanical properties as metals, accounts for the increased industrial applications of PPHZ in the fields of machine, aviation, spaceflight, electron, and electrical engineering since its discovery in the 1970s.[16] As a kind of aromatic polyester of high crystallinity and insolubility in all organic solvents, PPHZ is prepared from *p*-hydroxy-benzoic acid and has a polymeric chain structure as below:
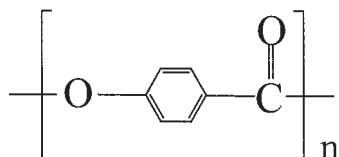
Scheme 1

We anticipate that the mixture of PPHZ and UHM-WPE might experience decomposition and molecular chain rearrangement during the compression molding and sintering process at elevated temperature, which could in turn contribute to increasing the interfacial linkage between the two polymer phases and hence improving the mechanical and tribological behaviors of the binary composites by combining the advantages of both polymers. Unfortunately, few reports have been available on the tribological behavior of UHM-WPE/PPHZ composites. Therefore, we prepared UH-MWPE/PPHZ composites and investigated the friction and wear behaviors of the composites.

EXPERIMENTAL

Materials and sample preparation

The UHMWPE powder (molecular weight: 3.5×10^6 g/mol) was produced by Beijing Second Factory of Auxiliary Agents (Beijing, China). The PPHZ powders with a grit size of 200 mesh were purchased from the ZhongHao ChenGuang Research Institute of Chemical Industry (Zigong, China).

Prior to mixing, PPHZ and UHMWPE powders were dried in an oven at 80°C for 240 min. The dried powders were mixed in a high-speed mixer. The resulting mixture was heated at 180°C for 90 min and then molded into a plate of $6 \times 7 \times 30$ mm³ under a pressure of 20 MPa. The composite plates to be tested were obtained after cooling of the molded specimens in ambient air. To determine the optimal volume fraction of the PPHZ particulates in the UHMWPE/PPHZ composites, the volume fraction of the PPHZ powder in the composites was varied from 5 to 95%, based on a series of tentative compression molding and sintering tests. It was found in the tentative compression molding and sintering tests that the volume fraction of

the PPHZ particulates in the present work can be as high as 95%, which is much larger than that for conventional inorganic particulate fillers.[17] It was supposed that the extremely high volume fraction of the PPHZ in the UHMWPE/PPHZ composites could be related to two aspects. First, the molecules of organic PPHZ and UHMWPE had stronger intermolecular interactions, which made it possible for the two organic phases to have compact interfacial bonding and hence gave birth to a higher volume fraction of the particulate filler. Secondly, the PPHZ filler and the UHMWPE matrix could experience decomposition and molecular chain rearrangement during the compression molding and sintering at elevated temperature, which also contributed to increasing the interfacial linkage between the two polymeric phases and hence allowed the inclusion of PPHZ particulates of a larger volume fraction. Accordingly, it was suggested that the inorganic and organic particulate fillers would have different "saturated filling fractions" in the same polymeric matrix.

Evaluation of mechanical and tribological properties

The mechanical properties of the composites were determined on an INSTRON-1121 tester at room temperature and a crosshead speed of 50 mm/min, according to ISO 178-1993. The Rockwell hardness of the composite samples was determined on a Rockwell hardness tester (Model 156, Laiyang, China) at room temperature, according to ISO 2039/2–1981. An M-2000 friction and wear tester (Xuanhua Tester Factory, China) was used to examine the friction and wear behaviors of the UHMWPE/PPHZ composites sliding against SAE52100 steel in a block-on-ring configuration. The schematic diagram of the friction and wear tester is shown in Figure 1. The block specimens of a size $6 \times 7 \times 30$ mm³ were made of the UHM-WPE/PPHZ composites, and the counterpart rings of a diameter 40 mm and thickness 10 mm were made of SAE52100 steel. The friction and wear tests were conducted at normal loads from 200 N to 600 N, sliding velocities of 0.424 m/s and 0.856 m/s, and ambient temperature about 25°C.

Worn surface observation

The worn surfaces of the UHMWPE/PPHZ composite blocks and the counterpart steel rings were coated with a thin layer of gold to allow morphology observation on a JEOL-5600LV scanning electron microscope (SEM); a HITACHI-H600 transmittance electron microscope (TEM) was used to observe the microstructures of two typical UHMWPE/PPHZ composite samples.
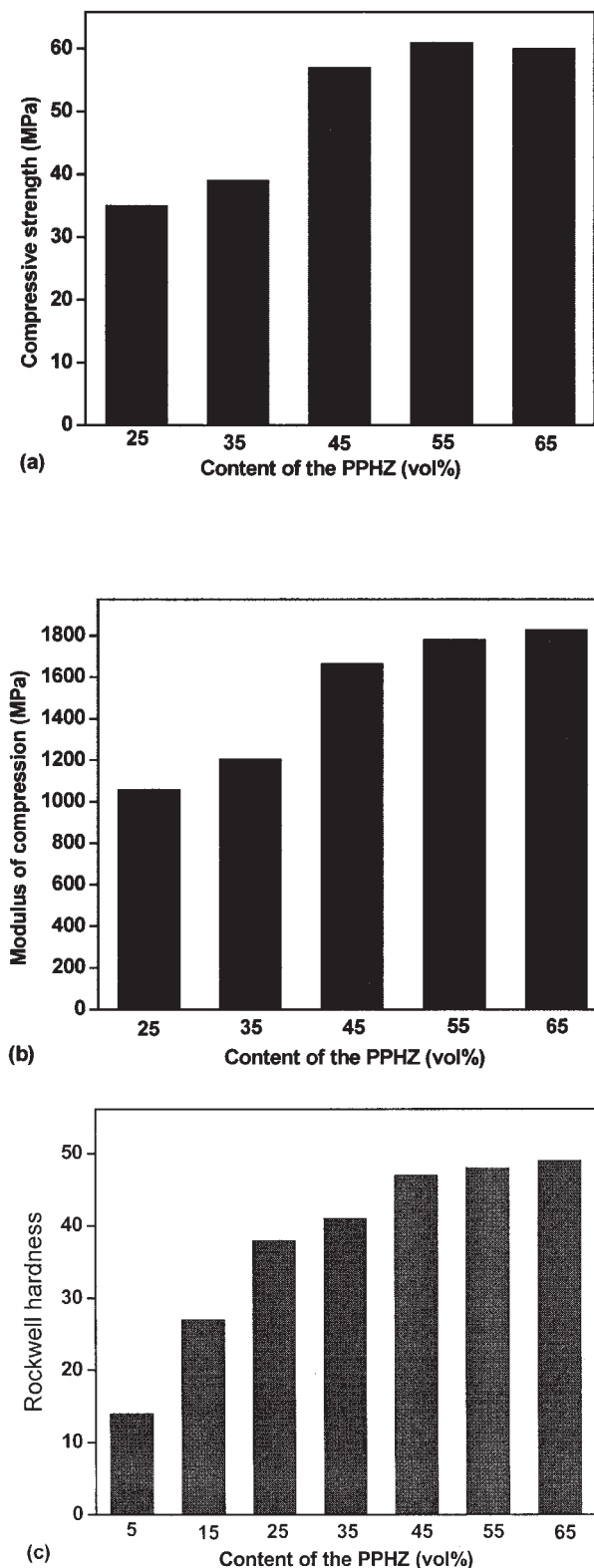
Figure 1 The mechanical properties of UHMWPE/PPHZ composites with various volume fractions of PPHZ. (a) Compressive strength, (b) Compression modulus, and (c) Rockwell hardness.

RESULTS AND DISCUSSION

Mechanical properties

Figure 1 shows the variation of the mechanical properties of UHMWPE/PPHZ composites with the volume fraction of the PPHZ. It is seen that all the compressive strength, compression modulus, and Rockwell hardness of the composites increase with increasing PPHZ content. This indicates that the inclusion of the PPHZ contributes to significantly reinforce the UHMWPE matrix, which may also account for the much better wear resistance of the filled composites than the UHMWPE matrix.

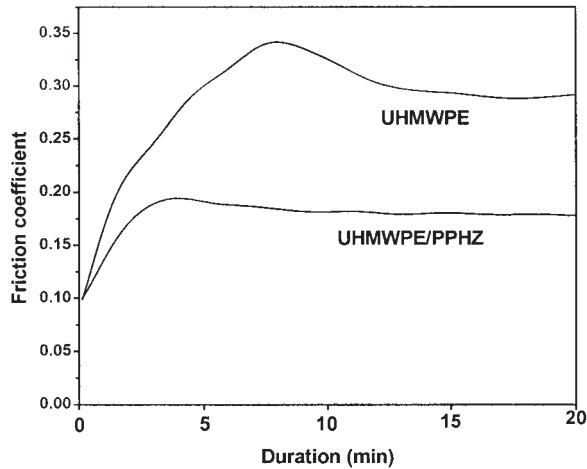### Friction and wear properties of UHMWPE/PPHZ composites

It is rationally determined that the PPHZ would exist as a discontinuous phase in the UHMWPE/PPHZ composites, since the compression molding and sintering of the mixed UHMWPE and PPHZ powders is carried out at 180°C, which is much lower than the softening point of the PPHZ. In other words, the PPHZ can be reckoned as a kind of particulate filler in the present work; thus, the variations in the friction and wear behaviors of the UHMWPE/PPHZ composites can be related to the filling function of the PPHZ particulates. Table I shows the friction coefficients and wear rates of the UHMWPE/PPHZ composites sliding against SAE52100 steel. Interestingly, though pure PPHZ registers a much higher friction coefficient than the pure UHMWPE, the inclusion of PPHZ in the UHMWPE leads to a decrease in the friction coefficients within a PPHZ volume fraction of 5–75%, while the friction coefficients assume smaller variations with increasing PPHZ content within that PPHZ volume fraction. This indicates that PPHZ may function to improve the self-lubricity of UHMWPE/PPHZ com-

TABLE I
Friction Coefficients and Wear Rates of UHMWPE/PPHZ Composites Sliding Against SAE52100 Steel Ring at 0.856 m/s and 200 N for 120 min

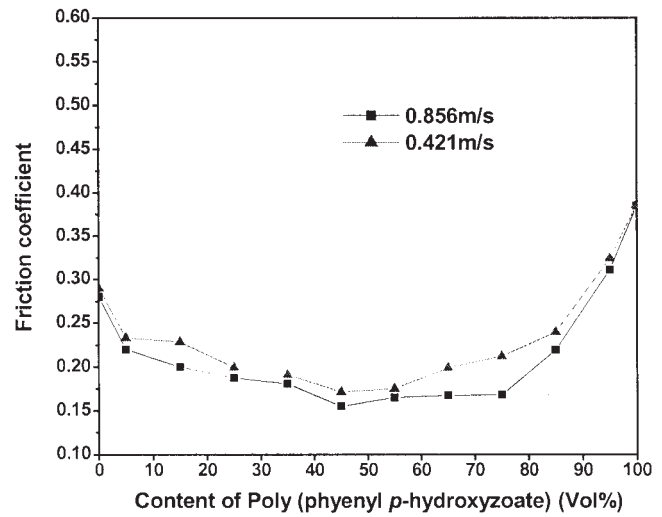| UHMWPE/PPHZ composition	Friction coefficient	Wear rate (10^{-5} mm^3 N^{-1} m^{-1})
100/0	0.28	52.4
95/5	0.22	45.9
85/15	0.20	44.1
75/25	0.19	3.96
65/35	0.18	1.76
55/45	0.16	0.40
45/55	0.17	0.42
35/65	0.17	0.43
25/75	0.17	0.46
15/85	0.27	5.2
05/95	0.31	12.1
0/100	0.39	24.6

**Figure 2** Typical friction curves of UHMWPE and UHM-WPE/65% PPHZ composite.

posites. Moreover, although PPHZ has much better wear resistance than the UHMWPE, its introduction at a smaller volume fraction (5%) leads to only a minor decrease in the wear rate of the UHMWPE/PPHZ. Even when the PPHZ volume fraction is as high as 15%, the wear rate of the UHMWPE/PPHZ composite is only decreased by less than 20%. Fortunately, the wear rate of the UHMWPE/PPHZ composite is strikingly decreased when the volume fraction of the PPHZ reaches 25%. And specifically, the smallest wear rate is recorded for the composites within a PPHZ volume fraction of 45–75%. However, when the volume fraction of the PPHZ is too much higher (above 85%), the composite assumes a considerable increase in the wear rate. This is because the interfacial interlocking between the UHMWPE matrix and PPHZ particulates is considerably decreased as the PPHZ proportion is too much higher. Namely, when the content of the PPHZ is less than 75%, the PPHZ particulates as the filler in the composite are able to be interlocked by the UHMWPE matrix and to support the load. However, when the content of the PPHZ exceeds 75%, the UHMWPE matrix cannot fully interlock the filler particulates of larger brittleness, which leads to deterioration in the wear resistance of the UHMWPE/PPHZ composites. Therefore, it is recommended that the PPHZ content be controlled within 45% ~ 75 vol % for maximal wear resistance.

Figure 2 shows the typical friction curves of UHMWPE and its composite with 65% PPHZ. It is seen that UHMWPE and the UHMWPE/PPHZ composite register increased friction coefficients with increased sliding duration during the running-in period, and they give relatively smaller steady-state friction coefficients at extended sliding duration. The friction coefficient for the UHMWPE during the running-in stage reaches a maximum as high as 0.33 at a sliding duration about

8 min, then it decreases gradually with increasing sliding duration and assumes a stable smaller value about 0.22 at an extended sliding duration of about 12 min. Contrary to the above, the UHMWPE/PPHZ composite has a greatly shortened running-in period (about 2 min) and assumes a smaller steady-state friction coefficient than the UHMWPE matrix. Since the friction and wear behaviors of polymers and their composites are closely related to their transfer onto the counterpart surfaces and the characteristics of the transfer films thereon,[17] it is inferred that the differences in the friction and wear behaviors of the UHM-

(a) Friction coefficients vs. PPHZ content
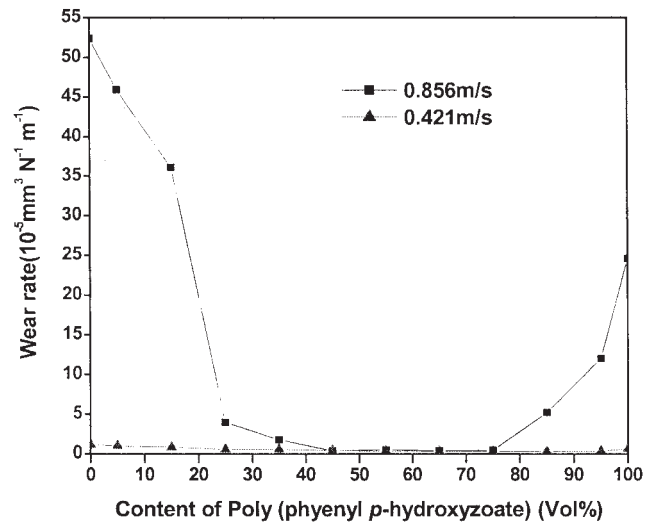
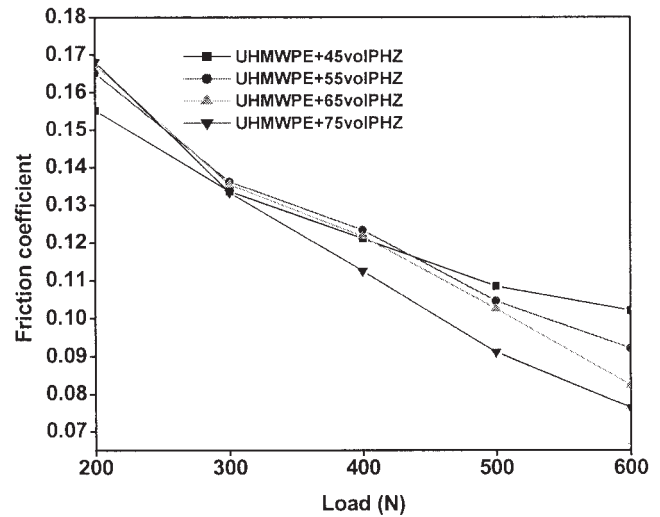(b) wear rates vs. PPHZ content

Figure 3 Variations of friction coefficients (a) and wear rates (b) of UHMWPE/PPHZ composites with the volume fraction of PPHZ at a normal load of 200 N and sliding velocities of 0.421 m/s and 0.856 m/s for a test duration of 120 min.

WPE and UHMWPE/PPHZ composite are attributed
to the effect of the PPHZ particulates on the transfer
behavior and the transfer film features of UHMWPE.
In other words, the PPHZ particulates help to speed
the transfer of the composite onto the counterpart steel
surface and the formation of a continuous and com-
pact transfer film thereon; thus, a smaller steady-state
friction coefficient is recorded for the UHMWPE/
PPHZ composite during a much shorter running-in
period, while the longer running-in period and larger
steady-state friction coefficient for the UHMWPE ma-
trix are determined by the slower transfer film forma-
tion and poorer continuity and compactness of the
transfer film. The above supposition could be rational
if one notes that the PPHZ particulates containing
polar groups (C=O) have strong chemical interaction
with the inorganic rubbing surface of the steel.

Figure 3 shows the variations of friction coefficients
and wear rates of UHMWPE/PPHZ composites with
the PPHZ content under a normal load of 200N and
sliding velocities of 0.421 m/s and 0.856 m/s. On one
hand, the inclusion of the PPHZ particulates leads to
decreases in the friction coefficients, and the friction
coefficients of the UHMWPE/PPHZ composites de-
crease with increasing PPHZ content until it reaches
about 45% (Fig. 2a). At a higher PPHZ content (above
45%), the friction coefficients assume increases with
increasing PPHZ content and even surpass that of the
unfilled UHMWPE. Besides, a minor difference is ob-
served in the friction coefficients at different sliding
velocities, which indicates that under the present test
conditions the friction-reducing behaviors of the UH-
MWPE/PPHZ composites are almost independent of
the sliding velocity. On the other hand, pure UHM-
WPE exhibits a much higher wear rate at a higher
sliding velocity than at a smaller one, while the wear
rates of the UHMWPE/PPHZ composites with differ-
ent compositions are almost unchanged with increas-
ing PPHZ proportions in the latter case (Fig. 3b). This
finding is similar to that observed for PTFE compos-
ites,[18] which shows that the wear-resistant abilities of
the UHMWPE/PPHZ composites are greatly depen-
dent on the sliding velocity. Interestingly, when the
PPHZ volume fraction is within 45% ~ 75%, almost
the same wear rates are observed at different sliding
velocities, which indicates that the composition of the
UHMWPE/PPHZ composites might dominate over
the sliding velocity in terms of the wear resistance.

Figure 4 shows the variations of the friction coeffi-
cients and wear rates of UHMWPE/PPHZ composites
with normal load at a sliding velocity of 0.856 m/s.
The friction coefficients for the four kinds of UHM-
WPE/PPHZ composites decrease with increasing ap-
plied normal load and reach the minimum at a normal
load of 600 N, while the composite filled with 75%
PPHZ has the lowest friction coefficient (Fig. 4a). This
indicates that PPHZ is more efficient for improving

(a) Friction coefficients vs. normal load
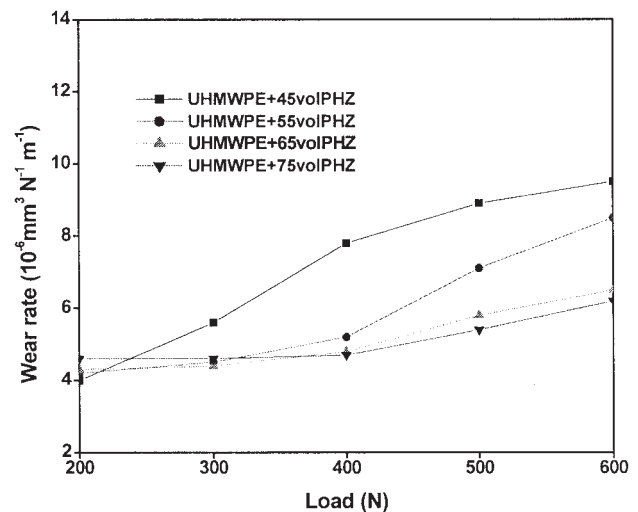
(b) Wear rates vs. normal load

Figure 4 Variations of the friction coefficients (a) and wear
rates (b) of UHMWPE/PPHZ composites with normal load
at a sliding velocity of 0.856 m/s and test duration of 120
min.

the friction-reducing behavior of the UHMWPE/
PPHZ composites at a higher load. We suppose that
the improved friction-reducing abilities of the UHM-
WPE/PPHZ composites at a larger normal load are
attributed to their enhanced viscoelastic deformation
therewith, which makes it possible to decrease the
friction by the viscoelastic flow of the polymer matrix
and the particulate filler. Contrary to the friction co-
efficients, as shown in Figure 4b, the wear rates of the
UHMWPE/PPHZ composites with various contents
of PPHZ increase with increasing load. This is related
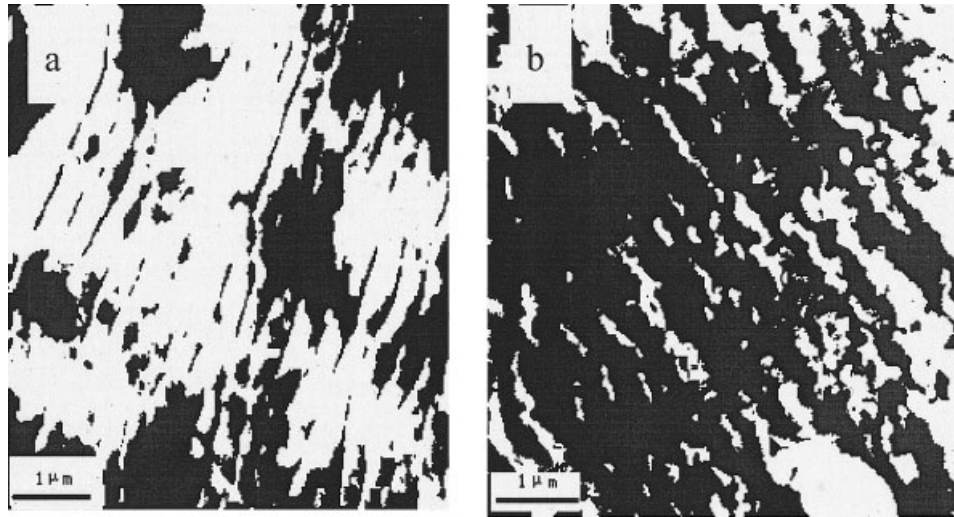to the more severe deformation-related destruction

Figure 5 TEM photographs of (a) UHMWPE/15% PPHZ composites and (b) UHMWPE/65% PPHZ composites.

and wear-related material removal of the composites at higher load. However, the UHMWPE/PPHZ composites of different PPHZ contents show different dependence on the normal load. Namely, the composites of relatively lower PPHZ contents are more sensitive to the normal load increasing, which is especially so for the UHMWPE/PPHZ composite containing 45% PPHZ. This implies that it would be feasible to improve the load-carrying capacity of the UHMWPE/PPHZ composites by controlling the PPHZ content to be high enough. The UHMWPE/PPHZ composites of

65% or 75% PPHZ assume a relatively minor increase in the wear rates with increasing load, which conforms to the excellent wear-resistance of the PPHZ.

Worn surface analysis

Figure 5 shows the TEM micrographs of two UHMWPE/PPHZ composites. It is interesting to note that there exist significant differences in the microstructures of the two UHMWPE/PPHZ composites. As the PPHZ content is smaller, the PPHZ particulates seem
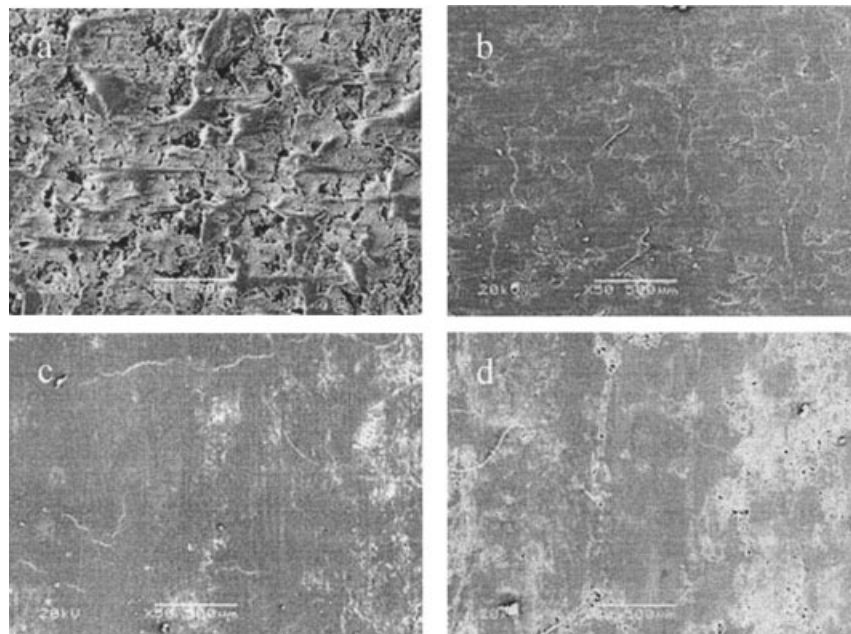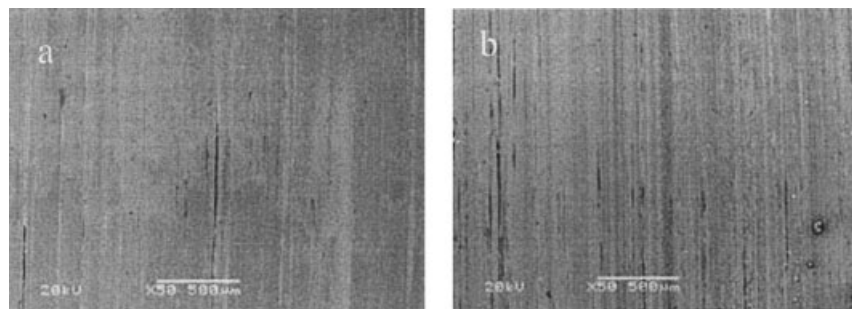

Figure 6 SEM pictures of (a) UHMWPE at 200 N and 0.856 m/s, (b) UHMWPE/65% PPHZ composite at 200 N and 0.856 m/s, (c) UHMWPE/65% PPHZ composite at 400 N and 0.856 m/s, and (d) UHMWPE/65% PPHZ composite at 600 N and 0.856 m/s. The test duration is 120 min.

Figure 7 SEM photographs of the worn surfaces of the steel ring sliding against (a) pure UHMWPE and (b) UHMWPE/ 65%PPHZ composite at a normal load of 200*N* and sliding velocity of 0.856m/s for 120min.

to be overwhelmed by the UHMWPE matrix (Fig. 5a) and distribute nonuniformly in the composite. In other words, the PPHZ particulates in this case are not able to fully carry the load and the deformation and wear is easier to originate in the weaker UHMWPE matrix of poorer mechanical (see Fig. 4) and wear-resistant properties. Contrary to the above, the UHM-WPE/PPHZ composite of a higher PPHZ content, as much as 65%, has much more uniformly distributed PPHZ particulates (Fig. 5b), which is beneficial for the PPHZ particulates to carry the load and improve the wear resistance. In other words, the UHMWPE matrix in this case is more strongly supported by the dispersed PPHZ particulates and hence shows better endurance to the load- and friction-induced deformation and damage.

Figure 6 shows the typical SEM micrographs of the worn surfaces of pure UHMWPE and UHMWPE/65% PPHZ composite at a sliding velocity of 0.856 m/s and normal loads of 200 N, 400 N, and 600 N. The worn surface of the pure UHMWPE shows deeper scratches and grooves, which is characterized by adhesion and friction-heat induced softening and plastic deformation (Fig. 6a). This conforms to the much poorer wear resistance of the UHMWPE matrix. Contrary to the above, the worn surfaces of the UHMWPE/65% PPHZ composite at various normal loads show dramatically decreased adhesion and plastic deformation (Figs. 6b, c, and d), and it is likely that a PPHZ-enriched layer of better uniformity at a modest load (400 N) is generated on the worn composite surface. This observation agrees well with the significantly increased wear resistance of the UHMWPE/PPHZ composite.

Figure 7 shows the SEM micrographs of the worn surfaces of the steel ring sliding against the pure UHM-WPE and the UHMWPE/65% PPHZ composite at a normal load of 200 N and sliding velocity of 0.856 m/s for 120 min. It is interesting to note that both the pure UHMWPE and the UHMWPE/65% PPHZ composite are able to form transfer films on the rubbing surface of the counterpart steel ring. However, the transfer film of the UHMWPE matrix seems to be thicker and incoherent (Fig. 7a), while that of the UHMWPE/ PPHZ composite appears to be thinner and coherent (Fig. 7b). It is thus inferred that the wear reduction of the UHMWPE/PPHZ composites is largely attributed to the enhanced adhesion of the transfer film onto the counterpart steel surface by the PPHZ particulates.
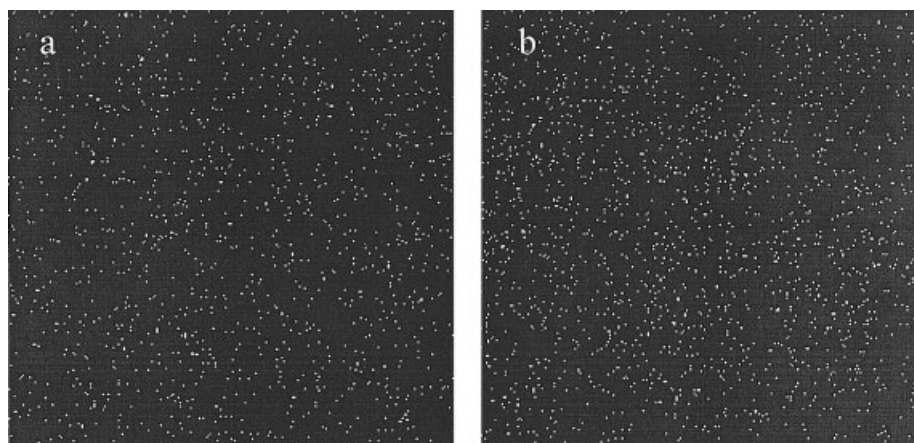
Figure 8 Fe elemental distributions on the worn steel surfaces rubbing against pure UHMWPE (a) and UHMWPE/65% PPHZ composite (b) at a normal load of 200 N and sliding velocity of 0.856 m/s for 120 min.

The difference in the transfer film features of the UHMWPE matrix and the UHMWPE/PPHZ composites is also demonstrated by the SEM images of the Fe elemental distributions on the worn steel surfaces rubbing against the UHMWPE matrix and the UHMWPE/PPHZ composite. As shown in Figure 8, more Fe elemental is observed on the worn steel surface rubbing against the UHMWPE/65% PPHZ composites (see Fig. 8b) than on that against the pure UHMWPE matrix (see Fig. 8a). In other words, the transfer film of the pure UHMWPE on the counterpart steel ring is thicker than that of the UHMWPE/PPHZ composites. This observation conforms well to the corresponding transfer film features of the UHMWPE matrix and the UHMWPE/PPHZ composites (see Fig. 7).

CONCLUSIONS

The incorporation of PPHZ particulates as the filler contributes to significantly improve the wear resistance of UHMWPE/PPHZ composites. The UHMWPE/PPHZ composites with volume fractions of the PPHZ particulates within 45% ~ 75% have the best wear-resistance in sliding against the steel ring. The friction coefficients of the UHMWPE/PPHZ composites decrease with increasing normal load and sliding velocity, which is attributed to the more severe softening and plastic deformation at larger load or sliding velocity. The wear rates of the UHMWPE/PPHZ composites increase with increasing load, and the composites of higher PPHZ content have better load-carrying capacity. The differences in the friction and wear behaviors of the UHMWPE matrix and the UHMWPE/PPHZ composites of various compositions are related

to their different mechanical strengths and microstructures and the transfer film characteristics on the counterpart steel surface. The PPHZ particulates contribute to increase the mechanical strengths and enhance the adhesion of the transfer film onto the counterpart steel surface, which largely accounts for the increased wear resistance of the UHMWPE/PPHZ composites.

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